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Control of the micrometric scale morphology of silicon nanowires through ion irradiation-induced metal dewetting

R. Lo Savio *, L. Repetto, P. Guida, E. Angeli, G. Firpo, A. Volpe, V. Ierardi, U. Valbusa

Physics Department and Nanomed Labs, Università di Genova, Via Dodecaneso 33, 16146 Genoa, Italy

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ABSTRACT

We propose ion-induced dewetting of Au thin films as a mechanism to modify and control the morphology of Si nanowires formed through metal-assisted chemical etching. We show that the patterns formed upon irradiation resemble those typical of dewetting phenomena, with a characteristic length in the nanometer range. Irradiated Au films are then used as a template for the fabrication of Si nanowires, and we show that a long-range order exists also in etched substrates, although at much longer length scales in the micrometer range. Investigation of the optical properties reveals that the Si nanowires emit broadband photoluminescence peaked at 700 nm. The proposed synthesis method allows tuning the morphological features of the nanowire bundles at the nanoscale without affecting the optical properties. This approach can be exploited for the engineering of nanowires-based devices where the morphological features become important.

1. Introduction

Microstructured silicon and silicon nanowires (Si NWs) attract a great interest in the scientific community for their peculiar properties determined by the quantum confinement effects that cannot be observed in the bulk counterpart and by the huge surface-to-volume ratio. They are studied as promising platforms for applications in several fields covering optoelectronics, photonics, photovoltaics, energy storage, and biosensing [1–5]. Many techniques are currently used for their fabrication, based either on bottom-up [6] or top-down approach [7]: among them Metal-Assisted Chemical Etching (MACE) is the most common, because it is simple, cheap, and suitable for large-scale manufacturing. In this process a crystalline Si substrate is partly coated with a noble metal and then immersed in a solution containing HF and an oxidative agent. Since the metal acts as a catalyzer for the chemical reactions, only metal-coated regions are removed; moreover, the etching is highly anisotropic and deep straight pores are formed. The resulting morphology can be therefore considered as a sort of extrusion of the two-dimensional surface distribution of the metal. A detailed and comprehensive review concerning this technique can be found in Ref. [7]. The morphology of Si NWs can be important to determine the physical properties, and potential applications: for example, for optoelectronic applications Si NWs must have a lateral size smaller than 10 nm in order to be optically active [8,9]; in biosensing applications the nanostructures are infiltrated with a liquid solution, and therefore both spatial arrangement and wettability of NWs are important features [10,11]. The morphology of Si NWs is directly determined by the distribution of the metal coating before the MACE, that in its turn can be controlled in several ways: varying the nominal film thickness [12,13], by thermal annealing [14,15], or through lithographic masks [16].

In this paper we propose the focused ion beam (FIB) as a processing technique to control the spatial distribution of Au on the substrate through dewetting, and we study how this affects the morphology of Si NWs obtained after the MACE. Previous attempts to use the FIB as a technique to modify and control the morphology of microstructured Si were limited to the FIB-assisted deposition of the metal coating on the substrate [17,18]. The Si NWs samples exhibit a spatial order in the μm-range, correlated to the characteristic nanometric lengths typical of dewetting phenomena appearing in ion-irradiated thin metal films.

2. Materials and methods

The synthesis protocol started with the deposition of an Au film with nominal thickness of 3 nm on a (100) p-doped (1–10 Ω cm) c-Si substrate by magnetron sputtering. Top-view images of the film surface acquired with a Scanning Electron Microscope (SEM) reveals that the film is not continuous, and uncoated substrate areas with

* Corresponding author.
E-mail addresses: roberto.lo.savio@edu.unige.it (R. Lo Savio), luca.repetto@unige.it (L. Repetto), patrizia.guida@unige.it (P. Guida), elena.angeli@unige.it (E. Angeli), giuseppe.firpo@unige.it (G. Firpo), andrea.volpe@edu.unige.it (A. Volpe), vincenzo.ierardi@unige.it (V. Ierardi), valbusa@fisica.unige.it (U. Valbusa).

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lateral size of ~5 nm and long up to ~200 nm are visible (Fig. 1a). Then, the film was irradiated with a 30 keV-Ga^+ beam in a dual FIB-SEM system (Zeiss 1540XB CrossBeam). Six rectangular regions (each one having a surface of $390 \times 290\ \mu m^2$) were irradiated by a rastering beam with fluences varying between 2.2×10^{12} and 7.0×10^{15} Ga/cm^2. Of course, after the ion irradiation Ga atoms are implanted in the substrate: however, even for the highest fluence we expect a concentration peak lower than 5 at%, located 30 nm below the Si surface [19]. During the irradiation the ion beam was defocused to a spot of ~2 μm in diameter, much larger than pixel size: this ensures a uniform irradiation all over the scanned surface. When a 30 keV Ga^+ ion impinges on the sample, the kinetic energy released around the point of impact may increase the temperature over the melting point and the irradiated region behaves as a liquid [20–23]: the film morphology is then determined by the dewetting, i.e. *the spontaneous withdrawal of a liquid film from a hostile surface* [24]. Indeed, ion-induced dewetting of thin metal film was previously reported [25–28]. Top-view SEM images in Fig. 1b and c show how the surface arrangement of Au is modified upon irradiation. The small uncoated regions in the as deposited film act as nucleation centers and enlarge under irradiation as a consequence of the formation of a molten area at their boundaries [28]: the film surface then appears as a network of Au interconnections. For increasing ion fluences, larger regions of the Si substrate are exposed until the connections disappear leaving only small isolated Au particles at the vertices surrounded by regions showing a very low contrast (above 2.0×10^{15} Ga/cm^2). Finally, after irradiation with the highest fluence, also the Au particles disappear and only a faint contrast remains visible on the substrate [13]. The observed evolution is compatible with dewetting through heterogeneous nucleation rather than spinodal mechanisms.

The irradiated samples were then used as a substrate for the fabrication of NWs through MACE; we used an aqueous solution containing HF and H_2O_2 with concentration of 12.8 M and 5.8 M, respectively. The sample was immersed in the solution for 15 min, then immediately rinsed with abundant deionized water, and finally dried with a N_2 flux. Top-view SEM image of the etched substrate, taken in the non-irradiated region, is shown in Fig. 1d: a cellular-like structure is clearly evident, with micrometric voids surrounded by thin walls formed by NWs bundles. Cross-section SEM images of the same sample are also reported in Fig. 1g and h: they reveal that NWs are $40 \pm 10\ \mu m$ long, and that near the surface they tend to bend and bundle together. By increasing the Ga^+ fluence, the walls become thicker with a consequent shrinking of the voids, thus resulting in a denser material (Fig. 1e and f).

3. Results and discussion

The fraction of un-coated substrate regions before the MACE and the surface fraction occupied by NWs bundles follow a common trend as a function of the Ga^+ fluence (Fig. 2a), as expected from the fact that etched substrate is an extrusion of the metal surface distribution. The surface fraction does not depend on the magnification used to acquire SEM images, confirming previous evidences that Si NWs samples are self-similar and that surface

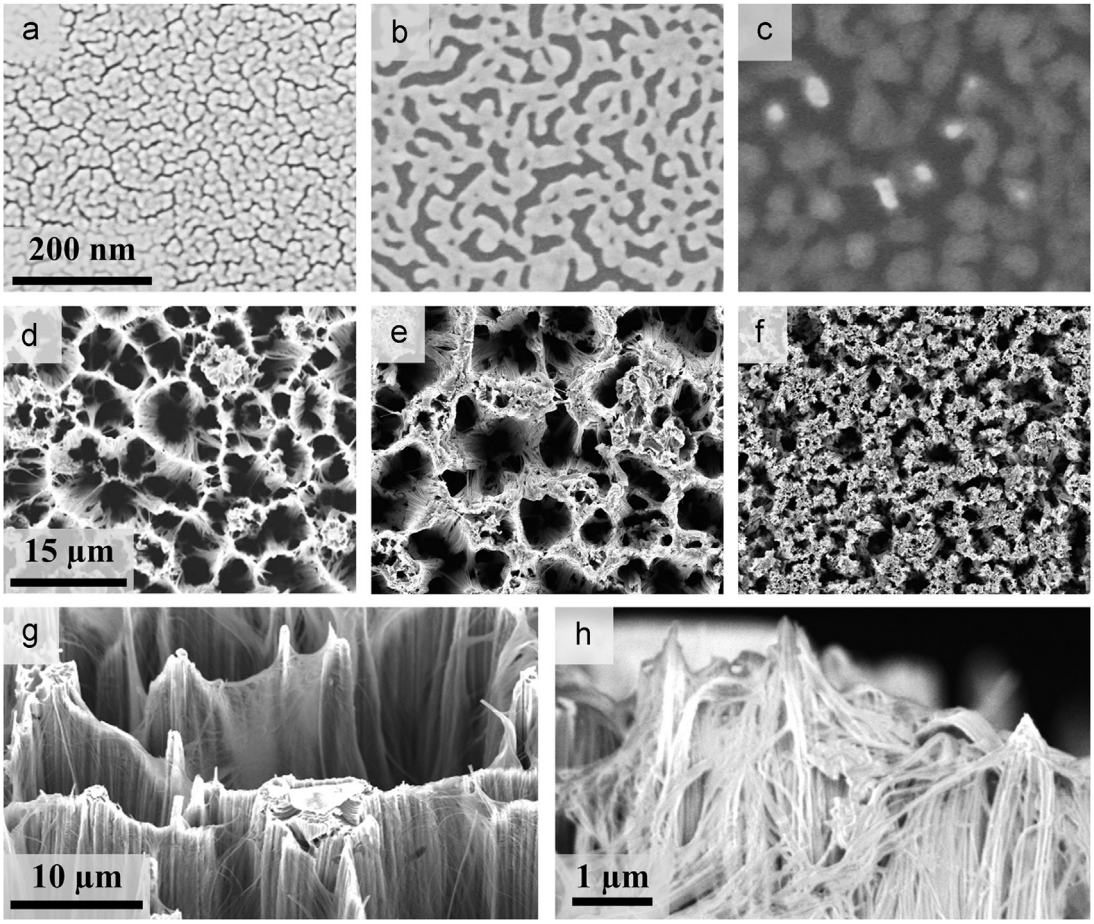

Fig. 1. Top-view SEM image of the Au film (a) before and after irradiation with 30 keV Ga^+ ions with a fluence of (b) 8.7×10^{13} at/cm^2, and (c) 1.7×10^{15} at/cm^2; the scale bar is the same for all the images in the row. (d)–(f) Top-view SEM images of the same films after chemical etching; the scale bar is the same for all the images in the row. (g) Tilted view of Si NWs in the non-irradiated region, and (h) cross-section image of the same sample acquired near the surface.